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Improved gas sensing performance of Al doped ZnO/CuO nanocomposite based ammonia gas sensor

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ABSTRACT

Pure ZnO nanoparticles (NPs), ZnO/CuO and Al-ZnO/CuO nanocomposites (NCs) were prepared using co-precipitation followed by sol–gel method. The structural and morphological properties of resulting materials were characterized by X-ray diffraction (XRD), micro Raman, high-resolution transmission electron microscope (HRTEM) and scanning electron microscope (SEM) respectively. The XRD results confirmed that the ZnO-CuO composite is formed without the presence of any ZnO-CuO alloy. The gas sensing performance of pure ZnO, ZnO/CuO and Al-ZnO/CuO nanocomposites towards ammonia gas at room temperature was investigated. The gas sensing results revealed that the Al-ZnO/CuO nanocomposite based gas sensor has superior gas sensing properties like, high response, good stability, and fast response (14 s) and recovery (9 s) time towards 500 ppm (parts per million) ammonia gas at room temperature compared to pure ZnO and ZnO/CuO based sensors. Further the gas sensing performance of Al-ZnO/CuO sensor towards different volatile organic compound (VOC) gases was tested.

1. Introduction

Ammonia is one of the widely using chemicals as a coolant in industries like automobile, chemical, textile, fertilizer, paper products and food industries [1,2]. A large amount of ammonia is releasing from industries in the form of aerosols and smog into environment. Ammonia is highly toxic gas and flammable at concentrations of 16–28% by volume in air. The acute exposure of ammonia causes strong irritating effect over our eyes, nose, mouth, lungs and throat. High dose of ammonia causes headache, vomiting, dyspnea, pneumonedema and even death [3,4]. According to the occupational safety and health administration (OSHA) the specified threshold limit value for ammonia in the work place is stipulated to 50 ppm [2]. Hence it is very essential to develop highly selective and reliable ammonia gas sensor for safety and process control in detecting environmental pollution.

At present, there are many monitoring methods in the detection of ammonia, like gas chromatography-mass spectrometry [5], optical spectroscopy [6] and electrochemical methods [7]. Compared to all the sensing methods metal oxide based electrochemical method is more attractive due to simple experimental procedures, fast response time, good stability and more over it is possible to build portable sensors. ZnO, SnO_2, WO_3, CuO, In_2O_3 and TiO_2 metal oxide gas sensors are widely studied [8–10]. Among these, ZnO based sensors are much attractive due to wide band gap with excellent electrical properties, non toxic, good chemical and thermal stability under standard operating environments and gained particular attention as promising sensor material for detection of different VOC vapors. A large amount of research has been made to enhance the gas sensing properties of ZnO such as changing the nanostructures, elemental doping and formation of heterostructures by different type of metal oxides.

Heterostructures made by metal oxides are more attractive due to the possibility of integrating physical and chemical properties. To date, many different metal oxide NCs have been reported, including ZnO/CuO nanoflakes for acetone detection [11], ZnO/CdS, ZnO/CdO core/shell nanorod arrays for ethanol detection [12], SnO_2/ZnO hetrostructured nanofibers for ethanol detection [13], In-(TiO_2/WO_3) nanohybrids for n-butanol detection, [14] ZnO/CdO composites for isopropanol detection [15], CuO-infiltrated ZnO composite for CO and H_2 detection [16], ZnO/In_2O_3 nanofibers for detection of trimethylamine [17], CuO/ZnO heterojunction for H_2S detection [18], ZnO/Co_3O_4 NCs for ethanol gas detection [19], SnO_2/ZnO nanofibers for methanol detection [16], SiO_2/SnO_2 nanofibers for H_2 and CO gas detection [20], PdO/SnO_2 hollow nanospheres for carbon monoxide detection [21], NiO/ZnO nanoplates for ethanol gas detection [22], Fe_2O_3/ZnO heterostructure for H_2S gas detection [23], NiO/WO_3 nanocomposites for high performance room temperature NO_2 sensors [24].

Recently some research groups have reported that ZnO/CuO NC based gas sensors show good gas sensing properties for different VOC

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gases. Apart from ZnO/CuO composites, lot of materials has been developed to detect ammonia gas; however the performance of these sensors is not up to the mark with respect to their response and recovery time. Hence it is required to develop the high response gas sensing materials to detect the ammonia gas very efficiently.

The present study focuses on further increase in the ammonia gas sensing properties of ZnO/CuO NC by advantage of doping. In this work Al-ZnO/CuO NCs were prepared using co-precipitation followed by sol–gel method. The structural, morphological and composition of the NCs have been characterized by XRD, micro Raman, HRTEM, SEM and energy dispersive spectroscopy (EDS). The gas sensing performance of Al-ZnO/CuO NC has been investigated by preparing porous film on alumina plate which contains silver electrodes. Gas sensing properties such as sensitivity, response, and response and recovery time have been evaluated and possible gas sensing mechanism has been discussed.

2. Experimental

2.1. Materials

Copper (II) acetate ($Cu(CH_3COO)_2$) A.R grade with purity of 99% and zinc acetate dihydrate ($(CH_3OO)_2Zn$, $2H_2O$) A.R grade with purity of 99.5% were used as starting materials. The solvent used in the experiment was ethanol A.R grade with a purity of 99.9%. Monoethanolamine ($CH_2(OH)CH_2NH_2$) used as stabilizer. All the chemicals were procured from Himedia and used without further purification.

2.2. Synthesis of ZnO, ZnO/CuO and Al-ZnO/CuO NCs

To synthesize the ZnO nanoparticles, firstly zinc acetate dihydrate solution (50 ml, 0.2 M) was prepared by using zinc acetate dihydrate as solute and ethanol as solvent and monoethanolamine as a stabilizer. This solution was stirred at 70 °C for 1 h by using magnetic stirrer. 50 ml of distilled water was added to this solution, which results in the formation of precipitate. This precipitate was collected using filter paper and dried in electric bunsen burner at 300 °C for 2 h.

The ZnO/CuO NCs were prepared by two step sol gel method. The first step involves the formation of precipitate from zinc acetate dihydrate solution (25 ml, 0.2 M) same as mentioned above. In second step this precipitate was washed in copper (II) acetate solution (25 ml, 0.2 M) followed by drying it in electric bunsen burner at 300 °C for 2 h.

The Al doped ZnO/CuO NCs were prepared same as ZnO/CuO NCs but with the addition of required amount of aluminum nitrate to zinc acetate dihydrate solution just before the formation of the precipitate.

2.3. Fabrication of gas sensor

The gas sensor was fabricated as follows: the pure ZnO, ZnO/CuO and Al-ZnO/CuO NC powder were mixed separately with deionized water to form thick slurry, this slurry was carefully coated on the surface of a clean alumina plate (which contains two silver electrodes with 4 mm apart. The dimension of the plate is 5 × 8 × 1 mm). The coated film was dried on hot plate at 100 °C for 3 h. The sensing response was evaluated in custom made gas sensing setup consisting of air sealed glass chamber equipped with a heater, thermocouple and probes. The required concentration of gas was calculated according to static liquid gas distribution method, which was calculated by using the following formula [25].

$$C = \frac{22.4 \times \varnothing \times \rho \times V_l}{M \times V_2} \times 1000 \quad (1)$$

where C (ppm) is the target gas concentration, Ø is the required gas volume fraction, ρ (g ml^{-1}) is the density of the liquid, V_1 (μl) is the volume of liquid, V_2 (l) is the volume of the chamber, and M (g mol^{-1}) is the molecular weight of the liquid. The sensor response (S) was calculated as $S = R_{air}/R_{gas}$, where R_{air} and R_{gas} are the electrical resistances of the sensor in the air and tested gas, respectively. The time of response and recovery is defined as the time taken by the sensor to achieve 90% of the total voltage change in the case of adsorption and desorption, respectively. The schematic diagram of the gas sensing measuring circuit is shown in Fig. 1. In the process of gas sensing test the input voltage was set at 5 V. Test gas formed by evaporating the liquid that injected on the bottom surface of gas chamber (bottom contain heater plate) by a microsyringe. The output voltage was taken across virtual resistance which changes with the sensor resistance. The sensor resistance is depends on test gas and their concentration.

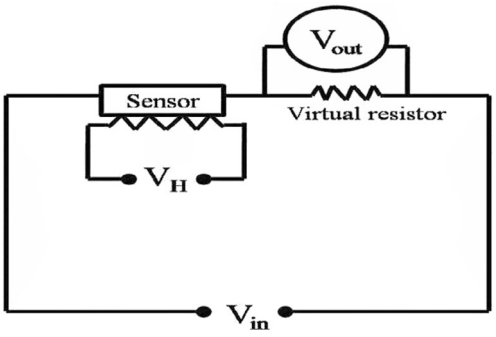

Fig. 1. The schematic diagram of the gas sensing measurement circuit.

3. Results and discussion

3.1. Structural analysis

The crystalline phase was confirmed by XRD. The XRD patterns of pure ZnO, ZnO/CuO and Al-ZnO/CuO nanocomposites were shown in Fig. 2. XRD pattern of ZnO contained the diffraction peaks at 2θ = 31.86°, 34.56°, 36.36°, 47.64°, 56.66°, 62.92°, 66.54°, 67.99°,and 69.16° which are assigned to reflection lines of (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0), (1 0 3), (2 0 0), (1 1 2) and (2 0 1) shows hexagonal wurtzite structure (JCPDS card number 89–0510). The XRD patterns of ZnO/CuO and Al-ZnO/CuO contain all the diffraction peaks of ZnO, in addition the spectra also contain diffraction peaks at 2θ = 32.60°, 35.59°, 38.82°, 48.80°, 53.59°, 58.34° and 61.58° which are assigned to reflection lines of (1 1 0), ($\bar{1}$ 1 1), (1 1 1), ($\bar{2}$ 0 2), (0 2 0), (2 0 2) and (1 1 3) show the monoclinic structure of CuO (JCPDS card number 89–5895) and don't have any diffraction peaks related to ZnO-CuO alloy phase, it reveals that the ZnO/CuO composite is formed. Further the XRD patterns of Al-ZnO/CuO show no shift in the peaks and no extra peaks related to Al were noticed. This indicates the doping of Al into ZnO doesn't affect the structure of ZnO.

The Raman spectra of pure ZnO nanoparticles, ZnO/CuO and Al-ZnO/CuO NCs in the range of wave number 100–1000 cm^{-1} were recorded at room temperature and shown in Fig. 3. The Raman spectrum of ZnO nanoparticles contains peaks at 330 and 438 cm^{-1}. The peak at 330 cm^{-1} is assigned as E_2 (high)–E_2 (low) modes and the peak at 438 cm^{-1} is assigned to E_2 (high) mode, these are the strongest and characteristic modes of wurtzite crystal structure of ZnO. Compared to pure ZnO nanoparticles, the Raman spectra of ZnO/CuO and Al-ZnO/CuO composite structures have additional peaks at 266, 293, 327 and 626 cm^{-1}. The peaks at 266 and 293 cm^{-1} correspond to the A_g mode, the peaks at 327 and 626 cm^{-1} correspond to the B_g mode, these are the strongest and characteristic modes of monoclinic structure of CuO. The Raman spectra of ZnO/CuO and Al-ZnO/CuO contain only peaks related to ZnO, CuO and no peaks observed related to ZnO-CuO alloy phase. It is indicating that the ZnO/CuO composite structure is formed. The Raman results were found to be in good agreement with XRD results.